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Digallane (4) Ga_2H_4 as the ideal gas phase equilibrium mixture of its six isomers [α]

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Abstract

A computational evaluation of relative stabilities and thermodynamics of six Ga_2H_4 isomers in an ideal gas phase has been carried out on the basis of recent quantum-chemical data (for two scalings of vibrational frequencies). Several interchanges of the relative stabilities with increasing temperature are reported. The ground-state structure is not the most stable species throughout. The relative stability interplay is reflected in the overall (i.e. belonging to the six-membered equilibrium mixture) thermodynamic functions of the system and in their isomerism contributions, especially in the temperature course (with a rather pronounced maximum) of the heat capacity terms. The vibrational frequency scaling does not influence the results substantially, particularly at higher temperatures.

INTRODUCTION

Quite recently, computational studies of gallium compounds have started to appear [1–6]. Particular interest has been devoted [5] to digallane (4), Ga_2H_4, and its isomerism was suggested. As previous computational studies [7–10] in isomeric chemistry demonstrated the possible pronounced thermodynamic effects of isomerism, it seems appropriate to submit the Ga_2H_4 system to a similar type of investigation.

SURVEY OF THE Ga_2H_4 ISOMERS

Altogether eight stationary points were found [5] on the Ga_2H_4 hypersurface (the highest energy approximation applied was the second order MP2 perturbation approach with a valence triply ζ basis set [11] with *d*-polarization functions). However, the geometry optimization and vibra-

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[α] Dedicated to Professor Robert Arnold Alberty on the occasion of his 70th birthday.

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TABLE 1

Survey of the relative energetics (kJ mol^{-1}) in the Ga_2H_4 system [a]

Symmetry	[No. (ref. 5)]	ΔE_i [b]	$\Delta H^{\circ}_{0,i}$ [c]	
			Scaling 1.0	Scaling 0.9
C_{3v}	[1]	0.0	0.0	0.0
C_{2v}	[2]	4.38	5.70	5.57
C_{3v}	[3]	64.1	61.2	61.5
D_{2d}	[4]	16.0	14.3	14.4
C_{3v}	[6]	58.5	55.8	56.1
C_s	[7]	55.2	52.2	52.5

[a] According to ref. 5; related to structure **1**.

[b] Potential energy difference with respect to structure **1**.

[c] Ground-state energy difference with respect to structure **1** (i.e. ΔE_i corrected for zero-point vibrations).

tional analysis were carried out only at the HF/3-21G* level. The vibrational analysis proved that only six of the eight stationary points were real local energy minima. Table 1 surveys the minima and their most sophisticated relative potential energies [5] (for simplicity, the original numbering [5] of the structures is used throughout this report). Two sets of vibrational frequencies are considered in the present study—the original [5] HF/3-21G* set (referred to as Scaling 1.0) and a derived one created through the suggested [5] scaling by a factor of 0.9 (Scaling 0.9). Addition of zero-point harmonic vibrational energy to the potential energy changes (i.e. transfer to the ground-state energy scale or, in thermochemical terms, to the zero-temperature enthalpy scale) does not influence the order of the isomers (Table 1).

ISOMERIC INTERPLAY COMPUTATION

The commonest way of incorporating temperature effects into relative stability reasoning consist in application of the so-called simple Boltzmann factors [12,13]. However, these Boltzmann factors are not convenient for our purpose, as they do not on principle admit an interchange in isomer stability order with changing temperature (the factors consider potential energy terms but not rotational–vibrational motions). Hence we shall follow a more sophisticated approach, considering [7–10] the rotational–vibrational motions of the individual isomers through their partition functions q_i, yielding the mole fractions of n isomers in their equilibrium mixture in the form

$$w_i = \frac{q_i \exp[-\Delta H^{\ominus}_{0,i}/(RT)]}{\sum_{j=1}^{n} q_j \exp[-\Delta H^{\ominus}_{0,j}/(RT)]} \tag{1}$$

where $\Delta H^{\ominus}_{0,i}$ denotes the ground-state energy terms related to one of the isomers as a reference structure. We shall follow a convention [9] that the species most stable in the low temperature region is taken as the reference isomer and assigned the index 1 (incidentally, the structure **1** in the Ga_2H_4 case; see Table 1). As usual [9], the partition functions q_i are of the rigid rotor and harmonic oscillator (RRHO) type.

Using the partition functions and energetics, the whole isomeric system thermodynamics can be described [7–10]. Two kinds of quantities are met with in this connection; namely, partial and overall terms. The standard partial terms $\Delta X_i^{\ominus}$ belong to processes dealing with the individual isomers, and the overall terms $\Delta X_T^{\ominus}$ to processes in which the equilibrium isomeric mixture acts as one pseudospecies. Finally, a third type of quantity has been introduced [8–10], namely, the so-called isomerism contributions to thermodynamic terms δX_1 related to the reference structure **1**, defined as

$$\delta X_1 = \Delta X_T^{\ominus} - \Delta X_1^{\ominus} \tag{2}$$

We shall consider three quantities X: enthalpy ($X = H$), entropy ($X = S$), and heat capacity at constant pressure ($X = C_p$). For example, it holds [14–16] for $X = C_p$

$$\delta C_{p,1} = \delta C_{p,w,1} + \frac{1}{RT^2}\left[\sum_{i=1}^{n} w_i\left(\Delta H_i^{\ominus} - \Delta H_1^{\ominus}\right)^2 - \left(\delta H_1\right)^2\right] \tag{3}$$

where $\delta C_{p,w,1}$ denotes the so-called isofractional [8,15,16] isomerism contribution to heat capacity

$$\delta C_{p,w,1} = \sum_{i=1}^{n} w_i\left(\Delta C_{p,i}^{\ominus} - \Delta C_{p,1}^{\ominus}\right) \tag{4}$$

and the isomerism contribution to enthalpy is given simply by [15]

$$\delta H_1 = \sum_{i=1}^{n} w_i\left(\Delta H_i^{\ominus} - \Delta H_1^{\ominus}\right) \tag{5}$$

The isofractional contribution (4) is in fact an auxiliary quantity; only the $\delta C_{p,1}$ term (3) considers the (frequently crucial) effects of changes in composition upon a temperature change accordingly. The latter term is therefore called the relaxation [8,15,16] isomerism contribution to heat capacity. (The isofractional contribution $\delta C_{p,w,1}$ ignores such temperature changes, and the relaxation term is reduced to the latter contribution if w_i values are considered to be temperature independent.)

RESULTS AND DISCUSSION

Figure 1 presents the temperature evolution of the RRHO mole fractions w_i in a broad temperature interval. Two sets of isomers are considered there —the full, six-membered set ("6") composed of all the six isomers of Table

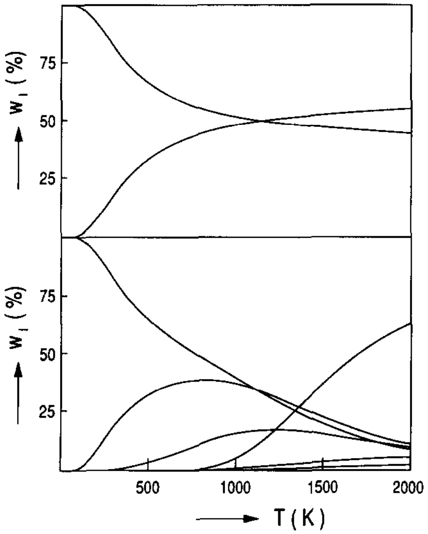

Fig. 1. Temperature dependences of the weight factors w_i of Ga_2H_4 isomers (scaling factor 1.0); upper part: set "2" composed of the species **1** and **2**, lower part: set "6" composed of all the six isomers. See Tables 1 and 2 (in the lower part the order of isomers at 1000 K reads (from top to bottom): **1**, **2**, **4**, **3**, **7**, **6**).

1, and a reduced one ("2") composed of only the two energetically lowest species **1** and **2**. The results from the two sets are significantly different, i.e. an inclusion of the higher species is important, too. Crossings of the curves (i.e. relative-stability interchanges) represent a striking feature of Fig. 1. Table 1 gives a specification of the relative-stability interchanges between the lowest **1** and **2** structures. In addition to the isomeric sets "6" and "2", also the remaining three reduced sets (created by recursive abandoning of the isomer with the highest identification number in each step starting from the "6" set; see Table 1) are considered for illustration. The temperature position of the crossing must be the same in all the five sets (under ideal-gas conditions); however, the related isomeric compositions can be quite different. However, the effect of vibrational-frequency scaling (Table 2) is almost negligible (it is actually a result of the high-temperature behaviour of the vibrational partition function [9]). Therefore, Fig. 1 (and also the other figures) deal with one scaling only, namely the scaling factor 1.0.

Figures 2 and 3 show the temperature dependences of the isomerism contribution to enthalpy δH_1 and to entropy δS_1 related to structure **1** as the reference structure. The figures present the dependences for the full, six-membered isomeric set and also for reduced isomeric sets created recursively by abandoning the isomer with the highest identification number in each step. Clearly enough, the reduced sets are rather formal ones—they would represent a special, reduced inter-isomeric equilibrium. Moreover, other reduced sets are still clearly possible. Consideration of the reduced set is

TABLE 2

Characterization of the **1**/**2** relative stability [a] crossing for various dimensions *n* of the Ga_2H_4 isomeric set [b]

n	Scaling 1.0			Scaling 0.9		
	T (K)	w_1 (%)	$\delta C_{p,1}$ [c]	*T* (K)	w_1 (%)	$\delta C_{p,1}$ [c]
"2"	1160	50.0	0.36	1150	50.0	0.37
"3"	1160	41.5	49.7	1150	41.8	48.8
"4"	1160	34.0	41.0	1150	34.3	40.2
"5"	1160	33.9	41.8	1150	34.1	41.0
"6"	1160	33.2	43.8	1150	33.5	43.1

[a] See Table 1 and Fig. 1.

[b] Sets labelled "2", "3",...,"6" are composed of the first two, three,...,six isomers, respectively, surveyed in Table 1.

[c] Related to structure **1** (see Table 1); in J K^{-1} mol^{-1}.

mainly for illustrative or methodological reasons (although they can simulate a situation with some kinetically forbidden structures). It can be considered as another visualization of the contributions and role of the higher isomers. However, within our purely thermodynamic framework, the full, six-membered set is the most important. Figures 2 and 3 indicate that the isomerism contributions to enthalpy and entropy can be really important. In other words, a simulation of the whole Ga_2H_4 system thermodynamics by the

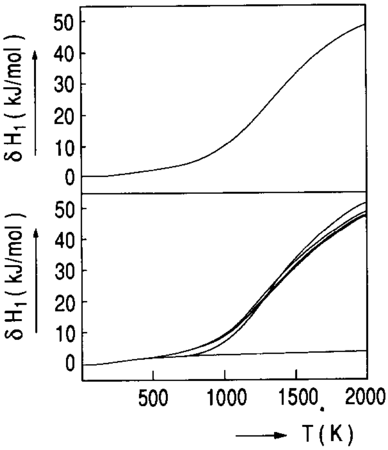

Fig. 2. Temperature dependences of the isomerism contribution to enthalpy δH_1 for Ga_2H_4 (scaling factor 1.0) isomeric systems (the contributions are related to structure **1** as the reference structure; see Table 1). The upper part belongs to the full, six-membered isomeric set; the lower part depicts dependences for the full and for reduced isomeric sets created recursively by abandoning the isomer with the highest identification number (Table 1) in each step (in the lower part, the order of the sets at 2000 K reads (from top to bottom): "3", "6", "5", "4", "2"; see Table 2).

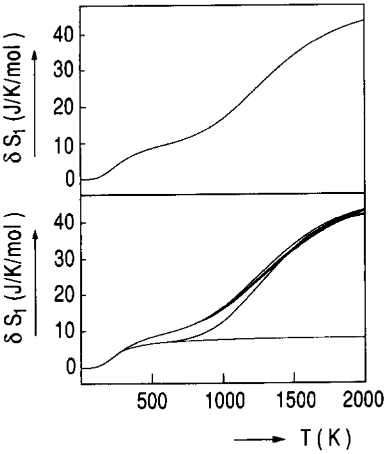

Fig. 3. Temperature dependences of the isomerism contribution to entropy δS_1 for Ga_2H_4 (scaling factor 1.0) isomeric systems (the contributions are related to **1** as the reference structure; see Table 1). The upper part belongs to the full, six-membered isomeric set; the lower part depicts dependences for the full and for reduced isomeric sets created recursively by abandoning the isomer with the highest identification number (Table 1) in each step (in the lower part the order of the sets at 2000 K reads (from top to bottom): "6", "3", "5", "4", "2"; see Table 2).

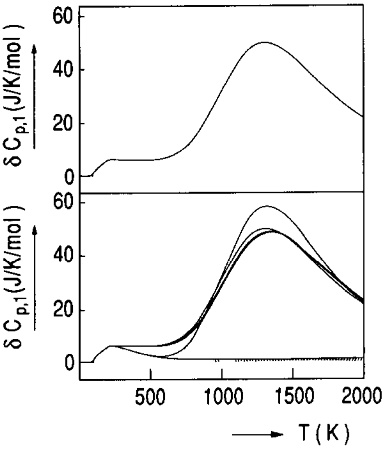

Fig. 4. Temperature dependences of the isomerism contribution to heat capacity at constant pressure $\delta C_{p,1}$ (relaxation term) or $\delta C_{p,w,1}$ (isofractional term, broken lines) for Ga_2H_4 (scaling factor 1.0) isomeric systems (the contributions are related to **1** as the reference structure; see Table 1). The upper part belongs to the full, six-membered isomeric set; the lower part depicts dependences for the full and for reduced isomeric sets created recursively by abandoning the isomer with the highest identification number (Table 1) in each step (in the lower part the order of the solid lines at 1200 K reads (from top to bottom): "3", "6", "5", "4", "2"; see Table 2).

TABLE 3

Characterization of the maxima [a] in the isomerism contributions to heat capacity $\delta C_{p,1}$ [b] for various dimensions n of the Ga_2H_4 isomeric set [c]

n	Scaling 1.0			Scaling 0.9		
	T (K)	w_1 (%)	$\delta C_{p,1}$ [b]	T (K)	w_1 (%)	$\delta C_{p,1}$ [b]
First maximum						
"2"	240	89.2	6.14	234	89.3	6.07
"3"	240	89.2	6.14	234	89.3	6.07
"4"	266	86.1	6.54	258	86.5	6.41
"5"	266	86.1	6.54	258	86.5	6.41
"6"	266	86.1	6.54	258	86.5	6.41
Second maximum						
"2"	–	–	–	–	–	–
"3"	1330	33.0	57.8	1330	32.9	57.8
"4"	1350	26.1	47.8	1350	26.0	47.7
"5"	1350	26.1	48.2	1350	26.0	48.1
"6"	1320	26.3	49.0	1320	26.2	48.9

[a] See Fig. 4.

[b] Related to structure **1** (cf. Table 1); in J K^{-1} mol^{-1}.

[c] Sets labelled by "2", "3",...,"6" are composed of the first two, three,...,six isomers, respectively, surveyed in Table 1.

partial terms belonging solely to structure **1** could be a quite poor approximation.

Figure 4 deals with temperature dependences of the isomerism contribution to heat capacity at constant pressure $\delta C_{p,1}$ (relaxation term) or $\delta C_{p,w,1}$ (isofractional term), again related to **1** as the reference species. As usual [15,16], the isofractional term turns out to be virtually negligible. The most interesting feature is represented by the temperature course with a maximum which is present with all relaxation terms (i.e. for the full six-membered set "6" and also for the reduced sets). Table 3 gives a more detailed specification of the maxima (both the small one at low temperatures and the pronounced one at higher temperatures). The height of the high-temperature maximum is quite substantial; however, the lower-temperature maximum is also significant for a precise evaluation of the system thermodynamics. Table 3 shows that the effect of vibrational scaling is for our purpose insignificant.

The isomerism contributions to thermodynamics cannot be measured directly. Thus, Fig. 5 presents the overall standard molar heat capacity at constant pressure for the equilibrium mixture of the six Ga_2H_4 isomers, $C_p^{\ominus}$, together with the partial term for structure **1** alone, $C_{p,1}^{\ominus}$. It is essentially important that the temperature maximum is preserved in the overall heat capacity term. Table 4 shows that the highest isomerism enhancement of the heat capacity can reach more than 28% for this system.

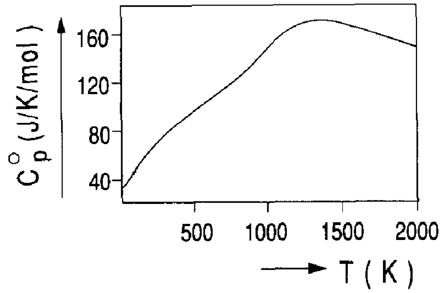

Fig. 5. Temperature dependences of the standard molar heat capacity at constant pressure for the equilibrium mixture of the six Ga_2H_4 (scaling factor 1.0) isomers ($C_p^\ominus$, solid line) and for structure 1 only ($C_{p,1}^\ominus$, the broken line; see Table 1).

This study serves as another interesting example of the quite large effects of isomeric interplay. Such interplay can be equally important for a future theory–experiment comparison as for the system equilibrium-behaviour prediction. There is still an open question concerning corrections with respect to deviations [17] from the RRHO model (currently, however, beyond computational possibilities). Anyhow, from the point of view of computational chemistry, the finding of a possible lower relative population of the global minimum (in some temperature regions) compared with some other (higher) local minimum is of clear interest. It should, however, be stressed that in a real system various decomposition reactions will take place, so that we shall actually deal with a complex reaction mixture containing in addition to Ga_2H_4 also such species as Ga_2H_2, Ga_2, Ga, H_2, or H. The absolute values of the isomeric mole fractions will be of course different in the complex mixture, although their relative values (under the ideal-gas phase presumption) will not be affected. In particular, the total

TABLE 4

Characterization of the maxima [a] in the overall heat capacity (max. $C_p^\ominus$) and in the relative contribution of $\delta C_{p,1}$ [b] to $C_p^\ominus$ (max. %) for the full (six-membered) Ga_2H_4 isomeric set [c]

n	type	T (K)	w_1 (%)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$\delta C_{p,1}/C_p^\ominus$ (%)
Scaling 1.0					
"6"	Max. $C_p^\ominus$	1360	24.7	171	28.5
"6"	Max. %	1310	26.9	170	28.7
Scaling 0.9					
"6"	Max. $C_p^\ominus$	1360	24.8	173	28.2
"6"	Max. %	1310	26.7	172	28.4

[a] See Fig. 5.

[b] Related to structure 1 (cf. Table 1); in J K^{-1} mol^{-1}.

[c] I.e., the set labelled "6" in Tables 2 and 3 and composed of all the six isomers presented in Table 1.

heat capacity term will be a still more complex quantity (so that our isomeric temperature effects may overlap).

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REFERENCES

1 K.D. Dobbs and W.J. Hehre, J. Comput. Chem., 7 (1986) 359.
2 V. Barone, C. Minichino, F. Lelj and N. Russo, J. Comput. Chem., 9 (1988) 518.
3 K. Lammertsma and J. Leszczyński, J. Chem. Soc., Chem. Commun., (1989) 1005.
4 K. Lammertsma and J. Leszczyński, J. Phys. Chem., 94 (1990) 2806.
5 K. Lammertsma and J. Leszczyński, J. Phys. Chem., 94 (1990) 5543.
6 B.J. Duke, J. Mol. Struct. (Theochem), 208 (1990) 197.
7 Z. Slanina, Int. J. Quantum Chem., 79 (1979) 79.
8 Z. Slanina, Thermochim. Acta, 78 (1984) 47.
9 Z. Slanina, Contemporary Theory of Chemical Isomerism, Academia, Prague and Reidel, Dordrecht, 1986.
10 Z. Slanina, Int. Rev. Phys. Chem., 6 (1987) 251.
11 S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai and H. Tatewaki, Gaussian Basis Sets for Molecular Calculations, Elsevier, New York, 1984.
12 K.S. Pitzer, J. Chem. Phys., 8 (1940) 711.
13 L. Piela, G. Némethy and H.A. Scheraga, J. Am. Chem. Soc., 109 (1987) 4477.
14 G.J. Mains, J.W. Larson and L.G. Hepler, J. Phys. Chem., 88 (1984) 1257.
15 Z. Slanina, Thermochim. Acta, 128 (1988) 157.
16 Z. Slanina, J. Phys. Chem., 92 (1988) 5836.
17 R.S. Berry, in R.G. Woolley (Ed.), Quantum Dynamics of Molecules, Plenum, New York, 1980.